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Fate of Monocrotophos in the Environment

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The fate of monocrotophos in the aqueous and soil environment was examined. Hydrolysis rates for monocrotophos are pH-dependent and follow first-order kinetics. The half-lives of monocrotophos in pH 3 and 9 buffer solution at 25 °C are 131 and 26 days, respectively. *N*-Methylacetoacetamide and *O*-desmethylmonocrotophos were the major hydrolytic degradation products detected. There was no observable qualitative or quantitative difference when the aqueous and soil experiments were conducted in the dark or with exposure to sunlight. Soil metabolism studies showed rapid and extensive decomposition of monocrotophos and its soil metabolites to $^{14}CO_2$ and unextractable residues. *N*-Methylacetoacetamide, *N*-(hydroxymethyl)monocrotophos, and 3-hydroxy-*N*-methylbutyramide were detected as soil degradation products. Soil TLC data indicated that monocrotophos was mobile under test conditions. Rotational crops planted at various time intervals after soil treatment contained low, if any, significant residue levels of monocrotophos or its metabolites.

Monocrotophos (1, 3-hydroxy-*N*-methyl-*cis*-crotonamide, dimethyl phosphate) is the active ingredient for Azodrin insecticide. Monocrotophos is active against a wide spectrum of phytophagous insects and mites (Corey et al., 1965). In addition to its high contact toxicity, monocrotophos also possesses systemic and residual activity when applied directly to the stems of the cotton plants (Bariola et al., 1970). Studies of the metabolic fate of monocrotophos have been conducted in plants (Menzer and Casida, 1965; Lindquist and Bull, 1967; Beynon and Wright, 1972), insects, and mammals (Menzer and Casida, 1965; Bull and Lindquist, 1966). However, there has been no published report on the detailed examination of the fate of monocrotophos in the environment. This report presents the study of the hydrolytic, photolytic, and soil degradation of monocrotophos. The soil-leaching and the accumulation potential of monocrotophos and its soil degradation products in various agricultural crops is also discussed.

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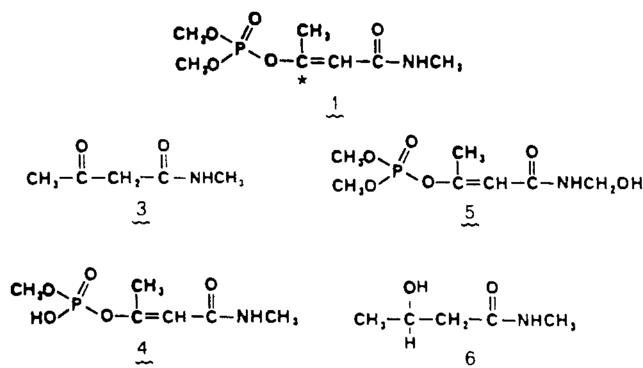

Figure 1. Chemical structure of monocrotophos and related degradation products. (Asterisk denotes carbon-14.)

EXPERIMENTAL SECTION

Radiosynthesis. Two different [^{14}C]monocrotophos preparations were used in this study. The first material was double-labeled with carbon-14 at the crotonamide 1- and 3-positions, and the second preparation was labeled with carbon-14 at the crotonamide 3-position only. They were synthesized by the condensation reaction of trimethyl phosphite and 2-chloro-*N*-methylacetoacetamide (**2**).

The radiosynthesis of [1,3-^{14}C]monocrotophos is described below in detail:

2 was prepared by the reaction of *N*-methyl[1,3-^{14}C]acetoacetamide (**3**; 279 mg, 2.4 mmol; 8.2 mCi; Dhom Product Ltd., North Hollywood, CA) in 2.5 mL of hexane and 1 mL of methylene chloride at reflux temperature with the dropwise addition of sulfuryl chloride (Aldrich Chemical Co.; 325 mg, 2.4 mmol; in 1.25 mL of hexane and 0.5 mL of methylene chloride). After the addition of sulfuryl chloride (during a 45-min period) was completed, the reaction was refluxed for 1 h. The solvent was removed, and the residual material was dissolved in 10 mL of methylene chloride and washed with saturated sodium bicarbonate. The organic phase was concentrated, and **2** (256 mg, 1.7 mmol, 71%) was purified by preparative thin-layer chromatography [1.0-mm silica gel TLC plate; E. Merck; ethyl acetate–tetrahydrofuran–methanol–water (14:5:3:3, v/v) as the developing solvent].

One drop of acetic acid, used as an isomer enhancer, was added to **2** (256 mg, 1.7 mmol; 5.5 mCi) in a final volume of 1 mL of benzene. To this reaction mixture was added 0.5 mL of trimethyl phosphite (Aldrich), and the reaction mixture was heated to reflux and kept at that temperature for 2 h. At the end of this period, another 0.5 mL of trimethyl phosphite was added and the reaction mixture was refluxed for an additional 1 h. The final product of **1** was purified by preparative TLC using the same solvent system as described above. The radiochemical purity and the specific activity of [1,3-^{14}C]monocrotophos were greater than 98.5% and 11.8 μCi/mg (2.6 mCi/mmol), respectively.

[3-^{14}C]Monocrotophos had the specific activity and radiochemical purity of 38.1 μCi/mg (8.5 mCi/mmol) and greater than 98%, respectively. Mass spectral and infrared data of [^{14}C]monocrotophos were consistent with those of the unlabeled reference standard.

Other reference standards were also synthesized at the Biological Sciences Research Center (BSRC), Shell Agricultural Chemical Co., Modesto, CA. These standards included *N*-methylacetoacetamide (**3**), *O*-desmethylmonocrotophos (**4**, 3-hydroxy-*N*-methylcrotonamide, methyl hydrogen phosphate), *N*-(hydroxymethyl)monocrotophos (**5**, 3-hydroxy-*N*-(hydroxymethyl)crotonamide, dimethyl phosphate), and 3-hydroxy-*N*-methylbutyramide (**6**). Their chemical structures are presented in Figure 1.

Chromatography and Radioassay. Radioactivity was quantitated in 15 mL of Aquasol-2 scintillation solution (New England Nuclear) with use of a Packard Model 300 liquid scintillation system. The radioactive area of the TLC plate, after solvent development and autoradiography, was removed by scraping and analyzed in an Aquasol-2/water (11 mL:4 mL) gel system. ^{14}C residues in the soil and crop samples were analyzed by combusting subsamples (100 mg) in a Packard 306 sample oxidizer. Combustion efficiency was determined on untreated samples and calibrated [1,3-^{14}C]monocrotophos solution as the internal standard. The oxidizer counting solution included a Carbosorb and Permafluor V (10 mL:12 mL) mixture.

^{14}C residues recovered from the soil and aqueous extracts were analyzed by two-dimensional TLC (silica gel F-254, 0.25 mm; E. Merck). The TLC R_f values and HPLC retention times of monocrotophos and model metabolites are presented in Table I. The distribution pattern of ^{14}C residues on the TLC plates were visualized by autoradiography on Kodak SB-5 single-coated X-ray film. Extractable radioactivity was also analyzed by high-performance liquid radiochromatography (RHPLC) (Varian Model 5000 liquid chromatograph) using a Partisil RP-1 column (5 μm, 5 mm × 10 cm). The mobile phase was composed of methanol–water (1:4, v/v) at the flow rate of 1 mL/min. Radioactivity was monitored by the FLO-ONE Model HP radioactive flow detector (Radiomatic Instruments and Chemical Co.).

Mass spectral analysis was carried out on the Finnigan 3200 GC mass spectrometer using a 12 m × 0.3 mm SE-30 WCOT glass column. Analysis was also carried out on the HP-5970A GC mass spectrometer (equipped with a mass-selective detector) using a 25 m × 0.2 mm fused-silica, wall-coated cross-linked 5% phenylmethylsilicone column. A summary of the mass spectral data of monocrotophos and model metabolites is also included in Table I.

Test Soils. Tujunga agricultural sand and Hanford sandy loam soils were obtained from Modesto, CA; Catlin silty loam and Piedmont sandy clay loam soils were obtained from West Burlington, IA, and Marietta, GA, respectively. The test soils were collected from a 0–15-cm depth from each location. Samples of each test soil were air-dried at room temperature for 24 h and screened to remove any particles larger than 2 mm prior to being analyzed for soil characteristics (Table II).

Hydrolysis Rate Determination. The hydrolysis rate was determined by monitoring the rate of disappearance of [1,3-^{14}C]monocrotophos in aqueous buffer solutions. These buffer solutions included pH 3 (0.01 M acetate buffer), pH 6 (0.01 M phosphate buffer), and pH 9 (0.02 M borate buffer). To ensure that the observed hydrolytic degradation was not caused by microorganisms, buffer solutions and all-glass apparatus were sterilized by autoclaving prior to the initiation of the hydrolysis experiment.

Hydrolysis studies were carried out at 25 and 35 °C in darkness. Aqueous solutions containing 25 ppm [1,3-^{14}C]monocrotophos were prepared in each type of sterilized buffer solution and distilled water (pH 6.6). Aliquots (0.25 mL) of the aqueous solutions were transferred to 1-mL sterilized ampoules, which were then sealed and placed in a Haake Model E-52 constant-temperature water bath equipped with a circulating pump. At zero time and at each time interval thereafter, duplicate samples (ampules) from each type of buffer solution were removed from the water bath and analyzed quantitatively and qualitatively. A 10-μL aliquot sample of the test solution was quantitated directly by liquid scintillation counting (LSC). In addition, the nature and the distribution of monocrotophos and its hydrolysis products were determined by TLC. A 10-μL aliquot of the aqueous solution was applied directly onto the TLC plates and analyzed by two-dimensional TLC.

An additional hydrolysis reaction was carried out with [1,3-^{14}C]monocrotophos (250 ppm) in pH 3 buffer at 35 °C for 45 days for the isolation and identification of the hydrolysis products. The hydrolysis sample (5-mL final volume) was extracted three times with an equal volume of chloroform. The combined organic phase was dried over anhydrous sodium sulfate, concentrated, and analyzed by TLC, GLC, and mass spectrometry (MS). To analyze the water-soluble products, the aqueous phase after chloroform extraction was freeze-dried and the residual material was resuspended in methanol, filtered, concentrated, reacted with diazomethane, and analyzed by TLC, GLC, and MS.

Aqueous Photolysis Rate Determination. The rate of photolysis was determined by monitoring the disappearance of [1,3-^{14}C]monocrotophos in aqueous solution at various time intervals after direct sunlight exposure.

Table I. TLC R_f Values and Mass Spectral Data of Monocrotophos and Model Metabolites

	TLC R_f value		HPLC:	
	system 1[a]	system 2[b]	(R_t, min)	mass spectral data: m/z
monocrotophos (1)	0.62	0.65	4.34	CIMS: 224 (M + H), 193, 157, 155, 127, 98 EIMS: 223 (M^+), 192, 164, 127, 109, 97, 79, 67, 59, 47, 43, 39
N-methylacetoacetamide (3)	0.52	0.58	1.23	CIMS: 116 (M + H), 98, 87, 85, 73 EIMS: 115 (M^+), 87, 85, 73, 69, 58, 55, 45
O-desmethylmonocrotophos (4)[c]	0.0	0.34		
N-(hydroxymethyl)monocrotophos (5)	0.43	0.55		CIMS: 210, 193, 167, 155, 127, 112, 84
3-hydroxy-N-methylbutyramide (6)	0.32	0.45		EIMS: 114 (M^+), 116, 112, 99, 73, 69, 58

[a] Dichloromethane–acetone–acetic acid (60:40:5). [b] Acetonitrile–water–ammonium hydroxide (40:9:1). [c] Analyzed as monocrotophos by GC/MS after methylation with diazomethane.

Table II. Characteristics of Test Soils[a]

	Tujunga sand (Modesto, CA)	Hanford loam (Modesto, CA)	Catlin loam (West Burlington, IA)	Piedmont loam (Marietta, GA)
cation-exchange capacity, mequiv/100 g	9.0	6.3	20.2	5.2
field moisture at $^1/_3$ bar, %	18.0	10.8	27.4	19.2
bulk density, g/cm^3	ND[b]	1.3	1.1	1.2
organic matter, %	0.35	1.1	2.0	1.5
pH (soil)	ND	6.7	5.3	6.4
pH (salt buffer)	4.8	ND	6.4	7.0
samd, %	84.6	64	19.6	52.0
silt, %	8.4	24	62.8	15.6
clay, %	7.0	12	27.6	32.4
texture	sand	sandy loam	silty clay loam	sandy clay loam

[a] Soils were analyzed by A & L Midwest Agricultural Laboratory, Inc., 11902 Elm St., Omaha, NB. [b] Not determined.

A 10-mL aliquot of distilled water (pH 6.6) containing 25 ppm [1,3-^{14}C]monocrotophos was transferred to an 11-mm-i.d. quartz glass tube. Test solutions were prepared in duplicate. Additional control sample tubes were wrapped in aluminum foil. Since differences in product and reaction rate may be observed between sensitized and unsensitized solutions, the photolysis experiment was conducted in natural water containing dissolved natural substances (e.g., fulvic and humic acids) that may be capable of sensitizing photochemical reactions. Natural water (pH 7.6) was collected from a nearby irrigation canal at BSRC and filtered through glass wool immediately prior to the initiation of the photolysis experiment. Sample tubes were placed outdoors throughout the 30-day test period in an area completely free of shade and reflections. Quartz tubes were placed on top of a black platform and were inclined at 30° from the vertical due north. This experiment was conducted from July 17 to Aug 18, 1979.

At zero time and at each time interval thereafter, 5-μL aliquots of the test solutions were quantitatively radioassayed by LSC and qualitatively analyzed by two-dimensional TLC by applying 5-μL aliquot directly onto TLC plates.

Soil Surface Photolysis. The photolytic degradation of [1,3-^{14}C]monocrotophos in the sterilized sandy loam soil surface was examined. A concentration of 5.0 ppm (μg/g) [1,3-^{14}C]monocrotophos was established in the test soil (350 g) by applying the appropriate amount of ^{14}C test material in methanol directly onto the soil surface. The treated soil was allowed to air-dry at room temperature before thorough mixing. A 25-g subsample of the treated soil was transferred to a glass Petri dish (150 × 25 mm) as a thin layer (<1 mm). Corresponding control samples were covered with aluminum foil. Exposed and control (dark) samples were placed together outdoors on the roof top in an open area throughout the 30-day test period. This experiment was conducted from July 24 to Aug 23, 1979.

To determine the chemical nature of the radioactivity recovered from the treated soil after various time intervals of sunlight exposure, soil samples (both exposed and control) were removed and extracted three times with 50 mL of an acetone–methanol (1:1, v/v) solvent mixture. The combined solvent extract was concentrated to approximately 2 mL, and the final volume was readjusted to 25 mL with saturated sodium chloride solution. This mixture was partitioned three times with 25 mL of chloroform. The combined chloroform extract was dried over anhydrous sodium sulfate, concentrated, and analyzed by two-dimensional TLC. Radioactivity remaining with the extracted soil was considered unextractable residues and were quantitated by oxygen combustion and LSC.

Aerobic and Anaerobic Soil Metabolism. Freshly collected sandy loam soil was used in this study. A concentration of 10 ppm [3-^{14}C]monocrotophos was established in air-dried (24-h) test soils by applying the appropriate amount of test material in water (8 mL/100 g) directly onto the soil surface. Treated soil samples (100 g each) were maintained in a 500-mL Erlenmeyer flask. The soil moisture level was adjusted to approximately 75% of the field moisture capacity. Soil samples were connected to an incubation system consisting of (1) a gas filter (to remove any CO_2 and gas impurities), (2) a 500-mL gas-washing bottle containing water (air humidifier), (3) manifold, (4) treated soil container, (5) a 250-mL gas-washing bottle containing 200 mL of ethylene glycol (volatile component trap), and (6) a 250-mL gas-washing bottle containing 200 mL of ethanolamine ($^{14}CO_2$ trap). Soil metabolism studies were conducted in darkness at 23 ± 1 °C.

In the aerobic soil metabolism study, [3-^{14}C]monocrotophos-treated soils were purged continuously with humidified air (20–30 mL/min). In the anaerobic soil metabolism study, soil samples were initially incubated under aerobic conditions for 6 days (1 half-life). Anaerobic conditions were established by waterlogging the soil container with 200 mL of tap water (2–3 cm above soil surface) followed by continuous purging of the soil container with humidified nitrogen.

Aliquots (2 mL) of the ethylene glycol and ethanolamine solution were sampled at various time intervals, and triplicate subsamples (0.5 mL) were assayed directly by LSC.

To examine the chemical nature of the soil residues, duplicate soil samples were removed at each time interval (aerobic study, immediately after application, 1, 2, 3, 4, 6, 11, and 16 days after treatment; anaerobic study, 10, 20, and 30 days after the establishment of anaerobic conditions) and extracted three times with 100 mL of 0.01 N calcium sulfate solution followed by a single extraction with 75 mL of acetone for 10 min each on a wrist-action shaker. The acetone extract was concentrated to approximately 10 mL, and the residual material was transferred to the aqueous soil extract. This aqueous mixture, after acidification to pH 3 with 1 N HCl, was saturated with sodium chloride and partitioned three times with equal volumes of chloroform. The combined chloroform extract was dried over anhydrous sodium sulfate, concentrated, and analyzed by TLC and RHPLC. Unextracted soil residues, after the aque-

ous and acetone extractions, were quantitated by LSC after combustion.

In the anaerobic metabolism study, flood water was separated from the soil sample by centrifugation. The water sample was freeze-dried, and the solid residual material was resuspended in methanol. Radioactivity associated with the methanol extract was analyzed directly by TLC and RHPLC. Radioactivity remaining in the anaerobically aged soil, after the removal of the water-logging fraction, was analyzed by the same soil extraction procedures as described above.

Soil-Leaching Studies. The soil-leaching potential of [1,3-^{14}C]monocrotophos and its soil degradation products were evaluated by soil TLC and adsorption/desorption studies.

[1,3-^{14}C]Monocrotophos at three different concentrations (0.1, 1, and 10 ppm) in aqueous 0.01 N calcium sulfate solution was prepared. Adsorption was determined by mixing a solution of [1,3-^{14}C]monocrotophos (10 mL) with soil (2.5 g) in a 4:1 volume to weight ratio. Each sample was run in duplicate. Screw-cap Pyrex tubes (16 × 125 mm) with Teflon-lined plastic caps were used as containers. Immediately after the addition of the solution, test tubes were vigorously agitated for 2 min on a Vortex mixer. Subsequent shaking was continued at a sufficient rate on a Labquake mixer to keep the soils in suspension. After equilibration (24 h in darkness at 25 ± 1 °C), the tubes were centrifuged at 2000 rpm for 15 min. Triplicate 0.25-mL aliquots of the supernatant were transferred from each tube into scintillation vials for direct radioassay.

Desorption was determined on the same samples used for the adsorption study, and the method was essentially the same. After 24-h equilibration of 2.5 g of soil sample with 10 mL of aqueous calcium sulfate–[1,3-^{14}C]monocrotophos solution, the suspension was centrifuged. Five milliliters of the aqueous solution was replaced with 5 mL of 0.01 N calcium sulfate solution, and the contents were shaken again on a Labquake mixer for 2 h followed by centrifugation. Five milliliters of the supernatant was again replaced with 5 mL of 0.01 N calcium sulfate. This process was repeated three times. After each centrifugation, radioactivity associated with the supernatant was radioassayed. Equilibrium adsorption and desorption isotherms for monocrotophos were described by the Freundlich equation.

The mobility of [1,3-^{14}C]monocrotophos was also examined by soil TLC. Four different test soils (sieved to remove particles greater than 0.5 mm) were used. Soil TLC plates were prepared by using a variable-thickness TLC spreader on a 20 × 20 cm glass plate. Distilled water was added to the sieved soil until a smooth, moderately fluid slurry was attained. The thickness of the soil layer was 0.75 mm for all test soils. Plates were air-dried for a minimum of 24 h after slurry application and were stored in a dry, dark location prior to use.

A horizontal line was scribed through the soil layer 11.5 cm above the base. [1,3-^{14}C]Monocrotophos and reference standard compounds, dichlorodi[U-^{14}C]phenyltrichloroethane (DDT), 2,4-dichlorophenoxy[2-^{14}C]acetic acid (2,4-D), trichloro[2-^{14}C]acetic acid (TCA), [^{14}C]triazine ring labeled atrazine, and 3-(3,4-dichloro-[U-^{14}C]phenyl)-1,1-dimethylurea (diuron), were spotted 1.5 cm from the bottom edge and 2 cm apart. Approximately the same quantities of test compounds (1–5 μg, 0.04–0.30 μCi) were used for each triplicate plate.

Soil TLC plates were immersed vertically in a closed TLC solvent tank containing 0.5 cm of water and were removed when the solvent front had migrated to the 11.5-cm line. Soil TLC plates after development were air-dried for 24 h, and the movement of the test chemical was determined from the autoradiogram. The soil TLC mobility was reported as the average frontal R_f of the spot or streak.

Rotational Crop Residue Study. A rotational crop study was conducted with [3-^{14}C]monocrotophos. Freshly collected sandy loam soil was packed to within 8 cm of the top of the 30-gal steel containers. A total of 30 such soil containers were prepared. Each soil container was treated with 60 mg of [3-^{14}C]monocrotophos in 500 mL of aqueous application solution (equivalent to approximately 3 lb/acre). The final specific activity of the treatment solution was 1.6 μCi/mg (0.36 mCi/mmol). This level of specific activity allowed for the minimum detection of 0.01 ppm [^{14}C]monocrotophos equivalent residues in the soil and various plant samples.

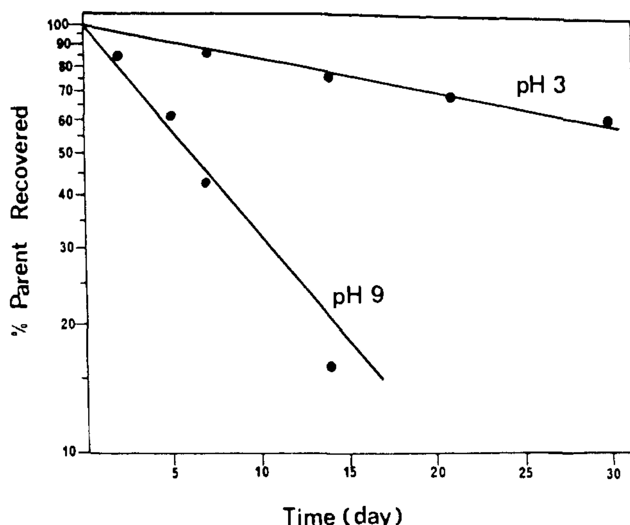

Figure 2. Hydrolysis rate of monocrotophos in pH 3 and 9 buffer solutions.

Table III. Hydrolysis Rate Constant (k_{hyd}) and Half-Life of Monocrotophos in Different Aqueous Systems at 25 and 35 °C

	$k_{hyd} \times 10^2$ day^{-1}		half-life, days	
aqueous system	25 °C	35 °C	25 °C	35 °C
pH 3	0.53	1.47	131	47
pH 6	0.52	2.09	134	33
pH 9	2.67	15.08	26	5
distilled water (pH 6.6)	0.50	2.77	139	25
natural water (pH 7.6)	0.47	2.38	147	29

Seeds of wheat (Anza), table beets (Detroit dark red) and leaf lettuce (Valmaine) were planted individually in separate soil containers at 30-day, 120-day, and 1-year intervals after soil application of [3-^{14}C]monocrotophos. Control crops were also plated individually in the untreated soil containers. The planting and fertilizing procedures followed acceptable agricultural practice. This rotational crop study was conducted under greenhouse conditions.

Both immature and mature crop samples were analyzed. The leafy portion of the lettuce, the aerial and the root portion of the beets and wheat straw, grain, and hulls were radioassayed for the level of total ^{14}C residues. Crop samples were homogenized and extracted with an aqueous–acetone solvent mixture. Extracted radioactivity levels from the crop samples and soil core samples collected at the planting and harvest intervals were examined.

RESULTS AND DISCUSSION

Hydrolytic and Aqueous Photolytic Degradation. The hydrolysis rates of monocrotophos are pH- and temperature-dependent. Reaction rates follow first-order kinetics (Figure 2) and are accelerated in alkaline solution. The calculated half-lives for monocrotophos at pH 3, 6, and 9 at 25 °C are 131, 134, and 26 days, respectively (Table III). There was no observable quantitative difference when monocrotophos was maintained in the sterilized or natural water. Ester cleavage product [*N*-methylacetoacetamide (**3**)] and the O-dealkylation product [*O*-desmethylmonocrotophos (**4**)] were identified as primary hydrolysis products by cochromatography with authentic standards and GC/MS. Hydrolysis product **4** was identified as monocrotophos (**1**) after methylation with diazomethane. The quantitative distribution of these hydrolysis products differed for the various buffer solutions tested (Table IV). A quantitative difference in the amount of the O-dealkylation product (**4**) between the acidic, neutral, or alkaline solution was not observed, and

Table IV. Rate of Formation of *N*-Methylacetoacetamide (3) and *O*-Desmethylmonocrotophos (4) as Hydrolytic Degradation Products of Monocrotophos in Various Buffer Solutions after the Indicated Period of Hydrolysis at 25 and 35 °C

	% applied radioactivity recovered as							
	N-methylacetoacetamide				*O*-desmethylmonocrotophos			
	pH 3		pH 9		pH 3		pH 9	
day	25 °C	35 °C	25 °C	35 °C	25 °C	35 °C	25 °C	35 °C
7	<2	<2	13.5	41.3	4.2	12.7	4.6	14.1
14	<2	2.3	28.6	59.1	7.4	23.0	7.6	21.1
21	<2	3.5	33.3	63.2	10.2	29.8	11.8	24.0
30	<2	4.3	39.5	68.6	14.5	38.0	14.6	30.5

Table V. Distribution of Monocrotophos (1) and Degradation Products *N*-Methylacetoacetamide (3) and *O*-Desmethylmonocrotophos (4) in Distilled Water at Various Time Intervals under Dark and Light-Exposed Conditions

	% applied radioactivity					
	dark control			light exposed		
day	1	3	4	1	3	4
7	84.2	2.3	13.5	85.7	1.8	12.5
14	73.1	3.0	23.9	70.6	2.7	26.7
21	56.5	4.3	39.2	57.8	4.6	37.6
30	44.6	6.4	49.0	45.4	5.8	48.8

4 was the major product in the acidic and neutral solutions. However, the cleavage of the phosphorus-crotonamide linkage to yield *N*-methylacetoacetamide was clearly predominant in alkaline solutions.

Hydrolysis and aqueous photolysis studies showed the rapid degradation of monocrotophos in the aqueous environment. Degradation rate and the chemical nature of the degradation products were not affected by exposure of the test solutions to the sunlight (Table V), nor were there significant differences in results from experiments run in distilled and in natural water. The half-lives of monocrotophos in the distilled water (pH 6.6) under the dark and light-exposed conditions at 25 °C were both approximately 24 days. Within the environmental pH range, *O*-desmethylmonocrotophos is the major aqueous degradation product of monocrotophos since approximately 50% of the applied radioactivity was recovered as 4 after 30 days.

Soil Surface Photolysis. A rapid dissipation of monocrotophos from the sunlight-exposed soil surface was observed. The half-lives of monocrotophos on the soil surface under the dark control and exposed samples were approximately 30 and 3 days, respectively. After 30 days, 45 and 3% of the applied radioactivity were recovered as the undegraded parent from the control (dark) and light-exposed soil samples, respectively. Dissipation data presented in Table VI suggest that the degradation of monocrotophos on the soil surface could be due primarily to microbial actions. This conclusion was based on the decline in the total recovery of the applied radioactivity in both the dark control and the exposed soil surfaces. This observation further suggests the microbial degradation of [^{14}C]monocrotophos to $^{14}CO_2$ (which was not monitored in this experiment). Microbial population was reestablished rapidly since the sterilized soil surface was directly exposed to the environment. *N*-Methylacetoacetamide and desmethylmonocrotophos were identified; however, they represented less than 3% of the applied radioactivity that could be recovered by solvent extraction. In addition to the potential loss of the applied radioactivity as $^{14}CO_2$, the majority of the ^{14}C residues in the 30-day sample (17 and 63% of the control and exposed soil surfaces, respectively) were characterized as unextractable residues not readily released by either aqueous or organic solvent extraction.

Soil Metabolism. Rapid degradation of [3-^{14}C]monocrotophos in the sandy loam soil under laboratory aerobic and anaerobic conditions was observed. Less than 7% of the applied [3-^{14}C]monocrotophos could be recovered after 16 days of aerobic incubation.

N-Methylacetoacetamide was detected as the only significant soil degradation product and was found mainly in the aerobic soil metabolism studies (up to 2% at day 6, Table VII). It dissipated rapidly and was not detected at the later sampling intervals. In the aerobically aged soil samples, several minor degradation products were also observed. However, each accounted for less than 1% of the applied radioactivity. Volatile metabolites were not detected. The majority of the applied radioactivity was recovered as $^{14}CO_2$ (accounting for up to 60%). Unextractable residues, accounting for up to 34%, could not readily be recovered by exhaustive extraction procedures with organic solvents (chloroform, ethyl acetate, acetone, methanol, acetonitrile) and water. Further fractionation showed the majority of these unextractable ^{14}C residues were associated within the fulvic acid fraction. Since monocrotophos and its degradation products decomposed readily under alkaline condition, the chemical nature of the released radioactivity in the fulvic acid fraction was not further characterized.

The initial degradation pathway for monocrotophos in the soil environment probably involved hydrolysis to generate *N*-methylacetoacetamide. This compound subsequently underwent rapid decomposition to yield $^{14}CO_2$ and intermediate metabolites that bound to soil macromolecules as unextractable residues. In addition, the generated $^{14}CO_2$ could be utilized by the soil microorganisms as a carbon source to form natural constituents not readily recovered by solvent extraction.

The metabolism of [^{14}C]monocrotophos in the sandy loam under laboratory anaerobic conditions was also examined. Treated soil was incubated under aerobic conditions for 1 half-life (6 days) prior to changing to anaerobic conditions. The dissipation rate of monocrotophos appeared to be reduced under anaerobic conditions (Figure 3); less than 6 and 21% of the applied [^{14}C]monocrotophos were recovered after 16 days of aerobic and anaerobic incubation, respectively. The calculated degradation rate constants for monocrotophos in the Hanford sandy loam under laboratory aerobic and anaerobic conditions were 0.17 and 0.09 day^{-1}, respectively. The half-lives of monocrotophos under aerobic and anaerobic conditions were approximately 4 and 8 days, respectively. In addition to *N*-methylacetoacetamide, 3-hydroxy-*N*-methylbutyramide (6) was recovered in the water-logging fraction under anaerobic conditions.

A comparative aerobic metabolism of [1,3-^{14}C]monocrotophos was also examined in the Catlin silty loam soil. A major difference between the sandy and the silty loam soils was not observed. However, *N*-(hydroxymethyl)-monocrotophos (5) was detected as a minor metabolite (4%), only in the earlier sampling interval (5 days post-

Table VI. Distribution of ^{14}C Residues on the Hanford Sandy Loam Soil TLC Plate after Direct Sunlight Exposure

	% applied radioactivity			
	zero time	7-day	14-day	30-day
extractable	96.6	27.2 (72.5)[a]	13.7 (67.9)	5.2 (47.6)
monocrotophos (1)	95.4	24.0 (71.3)	13.0 (62.5)	2.5 (45.4)
N-methylacetoacetamide (3)	ND[b]	0.8 (0.3)	ND (0.8)	0.5 (0.4)
O-desmethylmonocrotophos (4)	ND	1.0 (0.5)	0.3 (2.2)	1.4 (1.3)
unextractable	2.1	59.0 (11.3)	62.0 (13.8)	62.6 (16.9)
total	98.7	86.2 (83.8)	75.7 (81.7)	67.8 (64.5)

[a] Control sample. [b] Not detected.

Table VII. Distribution of ^{14}C Residues in the Hanford Sandy Loam Soil under Aerobic and Anaerobic Conditions

	% applied radioactivity										
		aerobic							anaerobic		
incubation time, days	zero time	1	2	3	4	6	11	16	16	26	36
$^{14}CO_2$		<1	<1	<1	4.4	9.3	32	47.8	33.6	43.5	50.6
water-logging phase									28.9	24.3	12.2
1									15.0	8.5	3.0
3									8.9	11.0	6.8
6									2.8	2.5	1.7
others[b]									2.2	2.3	0.7
total extractable	97.0	91.5	87.5	87.1	83.5	58.9	25.1	8.8	11.9	12.4	6.7
organic extractable	91.1	86.7	77.4	72.9	68.0	48.4	20.6	6.8	7.2	6.8	–
1	90.0	85.0	76.8	72.5	64.9	46.0	19.7	6.2	6.3	4.9	–
3	–[c]	–	–	–	1.3	1.6	0.9	–	0.4	1.3	–
others[b]	1.1	1.7	0.6	0.4	1.8	0.8	–	0.6	0.5	0.6	–
water soluble	5.9	4.8	10.1	14.2	15.5	10.5	4.5	2.0	4.7	5.6	–
unextractable	0.6	2.8	4.0	6.7	10.8	18.0	30.0	33.7	20.6	18.2	21.6
total recovery	97.6	94.3	91.5	93.8	98.7	86.2	87.1	90.3	95.0	98.4	91.1

[a] Anaerobic soil samples were incubated under aerobic conditions for 6 days prior to changing to anaerobic conditions. [b] To include all minor products. [c] Compound was not detected, or analysis was not carried out.

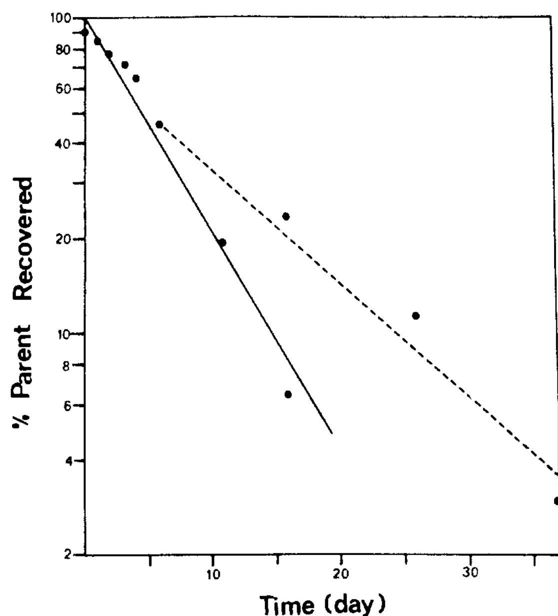

Figure 3. Degradation rate of monocrotophos in the Hanford sandy loam soil under aerobic (—) and anaerobic (- - -) conditions.

treatment) from the silty loam soil.

The effect and contribution of soil microorganisms to the degradation of monocrotophos was examined in the sterilized and nonsterilized sandy loam soils. Approximately 38% of the applied radioactivity was recovered as $^{14}CO_2$ from the nonsterilized soil sample at the end of the 30-day aerobic incubation period. In the sterilized soil samples, $^{14}CO_2$ was not detected and the majority of the applied radioactivity (>95%) was recovered as the undergraded parent molecule. Furthermore, unextractable residues were not detected in the sterilized soil samples.

Table VIII. Freundlich Equation Parameters[a] for the Soil Adsorption of Monocrotophos

	K	$1/n$	% adsorption	% desorption[b]
Tujunga agricultural sand	0.077	0.840	2–4	88–95
Hanford sandy loam	0.158	0.862	3–6	21–22
Catlin silty loam	0.615	0.976	11–15	65–69
Piedmont sandy clay loam	0.119	0.949	2–5	50–54

[a] Freundlich equation: $\log (X/M) = \log K = (1/n) \log C_e$. [b] Percent of the adsorbed materials recovered after the third desorption cycles.

Soil Mobility Potentials. The soil mobility of monocrotophos was evaluated by soil TLC and absorption/desorption studies.

The adsorption/desorption of monocrotophos was studied in four different test soils. Adsorption reached equilibrium in the Catlin silty loam soil in approximately 36 h. Monocrotophos was not adsorbed extensively in soil matters (2–13%). The Freundlich adsorption constants in the various test soils ranged from 0.08 to 0.62 (Table VIII). There is a direct correlation between adsorption and soil organic matter content. Adsorption was reversible, and 20–90% of the adsorbed material was released after the third desorption cycle.

Based on the mobility classification of Helling (1971), DDT (immobile), diuron (low), atrazine (intermediate), 2,4-D (mobile), and TCA (very mobile), soil TLC autoradiogram showed monocrotophos is mobile under this testing condition.

Rotational Crop Residue Study. A rotational crop study was conducted with [3-^{14}C]monocrotophos. The initial concentration of [3-^{14}C]monocrotophos in the 0–8-cm fraction of the soil container was 3.8 ppm, approximating the 3 lb/acre application rate. Lettuce, beets,

Table IX. Summary of the Distribution of Total [^{14}C]-Monocrotophos Residues in the Soil, Lettuce, Beets, and Wheat at Various Planting Intervals

	total [^{14}C]monocrotophos equivalent residues, μg/g		
	zero time	30-day	120-day
soil			
3–8 cm	3.83 ± 0.66[a] (18)[b]	1.91 ± 0.35 (6)	0.64 ± 0.16 (6)
8–15 cm	<0.04[c]	0.06 ± 0.05 (6)	<0.04 (4)
lettuce		0.02, 0.02[d]	<0.02, 0.02
beets			
leaf		0.03, 0.02	<0.01, <0.01
root		0.01, <0.01	<0.01, 0.01
wheat			
straw		0.13, 0.35	0.25, 0.29
hull		0.08, 0.11	0.04, 0.07
grain		<0.07, <0.07	<0.07, 0.09

[a] Mean ± standard deviation. [b] Number of samples mean was based upon. [c] Residue level below the limit of reliable measurement. [d] Residue data for the crop samples from each of the two soil containers.

and wheat planted 30 and 120 days after soil application were harvested at various growing stages and at maturity and were analyzed for total ^{14}C residues. A summary of the distribution of total [3-^{14}C]monocrotophos-equivalent residues (ppm) in the soil and the various crop samples is presented in Table IX.

Rapid dissipation of the applied [3-^{14}]monocrotophos was observed in the soil containers. The observed half-life of monocrotophos was approximately 15 days. At zero time and the 30-day planting time, approximately 92 and 23%, respectively, of the applied radioactivity were recovered as the undegraded [3-^{14}C]monocrotophos from the 0–8-cm soil depth. [3-^{14}C]Monocrotophos was not detected in the soil sample at the 120-day planting time. Significant degradation product, larger than 1% of the applied radioactivity, was not detected.

Monitoring the radioactivity in the various depths of the soil containers showed [3-^{14}C]monocrotophos and its degradation products had low soil mobility potential since the ^{14}C residues detected in the 8–15-cm level were negligible and represented only slightly above the quantitation limit of 0.04 ppm.

All lettuce, beets, and wheat grain from the 30- and 120-day planting intervals contained low levels of ^{14}C residues (from <0.01 to 0.03 ppm). Wheat straws contained the highest level of ^{14}C residues (approximately 0.25 ppm for both aging intervals). The majority of the wheat straw residues were organic-extractable materials composed of multicomponents as indicated by RHPLC analysis. No individual metabolites composing larger than 10% of the straw residues, or greater than 0.02 ppm [3-^{14}C]monocrotophos equivalent, were detected. These extractable residues (0.07–0.12 ppm), possibly radioactivity incorporated into natural plant components, were stable to enzyme, acid, and alkaline treatment. Results from this study showed rotational crops planted 30 and 120 days after treatment with monocrotophos did not contain significant residue levels of monocrotophos or its metabolites even at an exaggerated (3×) label use rate.

CONCLUSION

The fate of monocrotophos in the aqueous and soil environment was investigated. Under hydrolytic conditions, monocrotophos was degraded via O-dealkylation and ester cleavage to yield *N*-methylacetoacetamide and *O*-desmethylmonocrotophos. Monocrotophos degraded rapidly on the soil surface and in the soil under aerobic conditions. 3 and 6 were detected as soil degradation products. These products are not inhibitors of acetylcholinesterase nor do they exhibit insecticidal activities. In the soil environment, the crotonamide moiety of monocrotophos degraded rapidly and the majority of the applied radioactivity was recovered as $^{14}CO_2$ and soil-bound materials that could not be readily recovered by exhaustive solvent extraction. Monocrotophos and its soil degradation products (mainly unextractable materials) had no adverse effects on soil microbial populations (Rosenberg and Alexander, 1979) and enzyme functions (Shell Development Co., unpublished data). Monocrotophos was mobile as indicated by soil TLC. Because of its rapid degradation to unextractable materials, only a very limited amount of the soil-applied monocrotophos was available for plant uptake. Plant metabolism studies (Menzer and Casida, 1965; Lindquist and Bull, 1967; Beynon and Wright, 1972) reported the primary metabolic pathway of monocrotophos in plants involved the formation of small quantities of *O*-desmethylmonocrotophos, *N*-methylacetoacetamide, *N*-(hydroxymethyl)monocrotophos, and 3-hydroxy-*N*-methylbutyramide. The rotational crop study showed that very low, if any, residue of monocrotophos and its metabolites occurred in the plant grown in the monocrotophos-treated soil. Results from this study concluded that monocrotophos and its degradation products do not persist in the environment.

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